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The Application of a Natural Zeolite for Acid Mine Drainage Purification

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A natural zeolite from Serbia was employed for the removal of heavy metals from acid mine drainage (AMD) generated in the area of copper mine. The efficiency of the natural zeolite samples was tested on AMD that contained manganese, copper, zinc, nickel and cadmium ions in the concentrations above the maximal allowed, according to existing legislation. The results of X-ray diffraction (XRD) analyses of natural zeolite having a particle size of $-1 + 0.3$ mm, confirmed that the clinoptilolite ($Al_{1.6}H_{30}Ca_{2.06}O_{47.56}Si_{16.4}$) is a dominant mineral of mine tuff. A dynamic method was used for the experiments in order to simulate real conditions in an industrially relevant environment. The effect of the flow rate of AMD, type of columns and zeolite classes on the degree of adsorption of the heavy metals from AMD was investigated. The results of chemical analyses of treated AMD samples at a flow rate of 0.0033 $dm^3 s^{-1}$ which corresponds to the spontaneous outflow from the real accumulation indicate that concentrations of heavy metals are not decreased below that allowed for defined recipient class, except for copper. Also, these results show that the heavy metal ion removal serie for the industrially relevant environment can be given as: Cu > Zn > Cd > Mn > Ni. [doi:10.2320/matertrans.M2015292]

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1. Introduction

Pyrometallurgical method is most usual method for exploration of sulfide copper ore deposits.[1,2)] The AMD water is the result of the processes in copper mines (active or closed) when natural water percolates trough dumps, causing the pollution of both, waters and soil. Upon excavation, sulfide minerals are freely exposed to the atmospheric conditions and AMD waters are formed as a result of the oxidation processes. These waters contain heavy metals such as copper, cadmium, lead, manganese, bismuth, zinc, nickel and etc. Heavy metals are considered hazardous pollutants due to their toxicity, even in low concentrations. Therefore, it is necessary to reduce the heavy metal concentration in effluents and wastewater before discharging into the water bodies. The optimization of mine drainage purification processes require a development of new operations based on low-cost raw materials with high pollutant-removal efficiency.[3)] The complexity of effluents makes the process of heavy metals removal rather difficult, as well as the strict limitations that have been imposed to wastewater discharge everywhere in local water recipients. Among the methods such as neutralization/precipitation, oxidation, ultra-filtration, reverse osmosis, electrodialysis, using the low-cost adsorbents, ion exchange on natural zeolites seems to be a promising and attractive method.[4–7)] Natural zeolites are hydrated aluminosilicates of alkali and alkaline earth metals, which act as ion exchangers due to regularly arranged pores inside the crystals. Till date, it has been identified over 50 types from this group of minerals, of which the most important are: analcime, clinoptilolite, heulandite, filipsit.

Low-cost and easy available raw materials without any further economic investment are the very useful materials for any industrial use. The existence of active zeolite mine in Serbia, with estimated quantity between 500.000–800.000 t, which is only used for the agriculture and animal husbandry, was the main task for detail investigations of this material due to use for treatment of AMD generated in the area of copper mines in Serbia. The possibility of application the natural zeolite for heavy metal removal from original AMD water was investigated in laboratory conditions. The main task was purified water for safely discharge into defined III water class recipient, river Mali Pek.[8)] The experiments are realized in dynamic conditions; in a polypropylene (PP) columns filled by natural zeolite of different particle sizes, at different water flow rates similar to spontaneous processing parameters in real environmental conditions.

2. Experimental Procedure

Dynamic method was applied in the experiments with the real AMD samples in order to remove the heavy metals by using the samples of natural zeolite as adsorbent. Water treatment experiments were conducted in two types of PP columns. The characteristics of type 1 column, two pieces: 44 mm inner diameter and 500 mm active height, and type 2 column, one piece: 44 mm inner diameter and 800 mm active height. Investigations with the columns of different heights had to enable the experimental conditions similar to industrially achievable in the particular case of investigated samples. Three experimental series were performed: *First series:* using type 1 columns, *Second series:* using type 1 columns with zeolite filling of different type with respect to the zeolite used in the *First series* and *Third series:* using type 2 column with samples of natural zeolite as filling. Range of zeolite size classes was: $-5 + 2$ mm, $-2 + 1$ mm and $-1 + 0.3$ mm. The marks: (−) and (+) define the particle size range of the natural zeolite where (−) is the mark for 100% smaller grain size than specified value and (+) is mark for 100% larger grain size than specified value.

Zeolite particle size, height of the column filling and filled mass for the each experimental series were adjusted as follows:

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First series - the zeolite filling of the type 1 column was: layer I-particle size: $-5+2$ mm, mass: 61.9 g; layer II-particle size: $-2+1$ mm, height: 70 mm from the top of the layer I, mass: 84.7 g; layer III-particle size: $-1+0.3$ mm, height: 400 mm from the top of the layer II, mass: 420.7 g.

Second series - Extremely low flow rate in *First series* has demanded the verification of mass participation the zeolite fraction $-1+0.3$ mm in whole samples. Results have shown that almost 20 mass% was finer than 0.3 mm. Fractions finer than 0.3 mm were removed after sieving. Filling of type 1 column was carried out in the following way: layer I–particle size: $-5+2$ mm, mass: 41 g; layer II-particle size: $-2+1$ mm, height: 70 mm from the top of the layer I, mass: 60 g; layer III-particle size: $-1+0.3$ mm, height: 400 mm from the top of the layer II, mass: cca 360 g.

Third series - Zeolite classes and filling height of the type 2 column were arranged in the following way: layer I–particle size: $-5+2$ mm, mass: 47.6 g; layer II-particle size: $-2+1$ mm, height: cca 30 mm from the top of layer I, mass: 39.1 g and layer III-particle size: $-1+0.3$ mm, on the height of 750 mm from the top of layer II, mass 1000 g. Zeolite class that have been used was previously sieved trough the sieve of $-1+0.3$ mm.

The volume of the AMD (1 dm^3 was flowed through the type 1 and 3 dm^3 through the type 2 column) that passed through the columns was measured by the graduated vessel that was positioned under the column.

The adsorption degree (AD in %) for the treated AMD samples can be calculated by the equation:[3)]

$$AD(\%) = (1 - C_t/C_i) \times 100 \quad (1)$$

Where: C_i and C_t are the initial and actual concentration (g dm^{-3}) of metal in AMD water sample, respectively.

Concentrations of various heavy metals were determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES) on SPECTRO CIROS VISION instrument. Gravimetric method was used for determination of suspended particles and dry residue. pH value was measured with pH meter PORTABLE (pHM80). The sieve analyses of zeolite samples were performed by standard sieving method, on TYLER sieves. Mineralogical characterization of the sample which particle size was $-1+0.3$ mm, is estimated by X-ray diffraction using GNR Explorer diffractometer under following conditions: Cu Ka at wavelength 1.54 Å, voltage $U = 40$ kV, current $I = 30$ mA. Detector: scintillation counter; geometry of the apparatus: θ-θ.

3. Results and Discussions

3.1 Materials characterization

3.1.1 Characterization of the AMD start sample

The origin AMD accumulated in abounded copper open pit was used without previous treatment. Based on the field measurements under different weather conditions, the discharged amount of AMD was estimated to 250 $dm^3\,s^{-1}$. Sample of 50 dm^3 of mine water was analyzed, and the results of the physical and chemical characterization are presented in Table 1.

The concentrations of manganese, zinc, copper, cadmium and nickel ions are above the MAC values, while the concentrations of arsenic and chromium ions were below the detection limit of the used chemical method. The iron and lead ions concentration were below the MAC values.

Table 1 Physico-chemical characteristics of the AMD.

Parameter	Identification of the sample	
	AMD sample	Maximal allowable concentrations (MAC) of III class surface waters[9,10)]
Mn, mg dm^{-3}	21.0	0.3
Zn, mg dm^{-3}	7.1	2
Cu, mg dm^{-3}	0.56	0.5
Fe, mg dm^{-3}	0.067	1
Cd, mg dm^{-3}	0.022	0.0006
As, mg dm^{-3}	<0.02	0.05
Cr, mg dm^{-3}	<0.005	0.1
Pb, mg dm^{-3}	0.014	0.014
Ni, mg dm^{-3}	0.19	0.034
Si, mg dm^{-3}	4.2	—
dry residue, mg dm^{-3}	3798	—
susp. particles, mg dm^{-3}	<5	—
pH	6.84	6.5–8.5

Table 2 Chemical composition (mass%) of natural zeolite.[11)]

Component										
SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3
62.30	12.59	0.23	1.20	4.08	1.94	0.70	0.63	0.016	0.22	0.05

3.1.2 Characterization of the natural zeolite

Chemical composition of the natural zeolite used in laboratory testing is presented in Table 2. The results of XRD analyses of natural zeolite show that the dominant mineral is low-crystallized clinoptilolite (approximately 55 mass%) with typical reflections ((*hkld*/Å: (020)–9.02; (200)–7.92; (201)–6.79; (131)–3.975; (330)–3.957, (222)–3.422, (151)–2,979. Other minerals with notable contents are: anorthite (approximately 40 mass%), with typical reflections (040)–3.213, (204)–3.198, (004)–3.191, and quartz (approximately 5 mass%) with typical reflections: (100)–4.26 and (011)–3.343 (Fig. 1 and Table 4).

3.2 Heavy metal removal from AMD by natural zeolite

Chemical composition of the AMD water samples after purification through the zeolite layers during the different experimental series is presented in Table 3.

Calculated value for the volumetric flow during the *First series* was 0.00018 $dm^3\,s^{-1}$ and this value is considerably lower than the value which should be expected in real spontaneous conditions. When recalculated this value to the required surface area for the adsorption, it is not applicable on the field. Upon passing 3 dm^3 AMD through the column, pH value of the effluent was 7.51. Flow-through speed of the water was 0.45 $m\,h^{-1}$, which is about 27 times slower than the expected value (128 $m\,h^{-1}$). Hence, the results of chemical analysis, given in Table 3, show that the purification is not satisfactory. The concentrations of Mn, Ni and Cd ions are still was higher than MAC values.

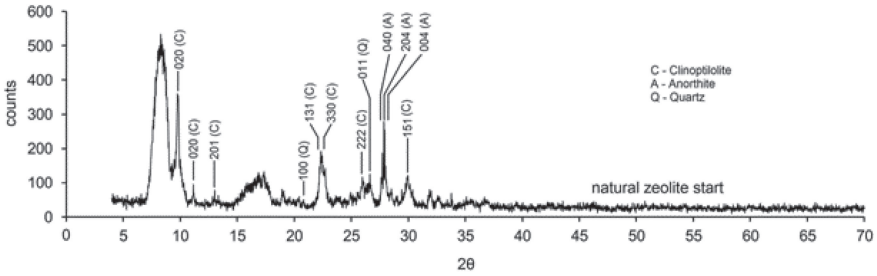

Fig. 1 X-ray diffraction pattern of natural zeolite sample.

Table 3 Chemical characterization of AMD after treatment with natural zeolite.

Parameter	First series	Second series	Third series	MAC of III class surface waters
Mn, mg dm^{-3}	2.8	16.5	11.2	0.3
Zn, mg dm^{-3}	0.051	3.5	0.034	2
Cu, mg dm^{-3}	0.023	0.044	0.037	0.5
Ni, mg dm^{-3}	0.14	0.17	0.15	0.034
Cd, mg dm^{-3}	0.001	0.012	0.004	0.0006
pH	7.51	6.12	7.62	6.5–8.5

The calculated value for the flow rate in the *Second series* was 0.0033 dm^3 s^{-1}, which correspond to flow-through speed of 8 m h^{-1} over area. The flow rate is 37.5% lower than the value expected in real spontaneous condition. Results for purified AMD sample show that only the Cu ions concentration is lower than MAC value. Lower pH values in comparison to the first experimental series indicate that contact time of AMD and zeolite was shorter. However, when Cu concentration from the first experimental series is compared to the second one, it follows that adsorption of Cu cations on zeolites is efficient even when much higher speed of filtering is applied.

During the *Third series*, the calculated AMD flow rate and flow-through speed were 0.00027 dm^3 s^{-1}and 0.65 m h^{-1}, respectively. The results from Table 3 show that only the Cu and Zn ions concentrations are lower than corresponding MAC value. The concentrations of Mn, Ni and Cd ions after the purification are even higher. pH values confirm that lower flow-through speed allows satisfactory values to be reached.

The calculated values (eq. (1)) of adsorption degrees for investigated elements are presented on Fig. 2. The ratio of heavy metals concentration in effluent and corresponding MAC value is presented on Fig. 3.

Concentration of the all investigated elements is decreased. Only for Cu, similar values for the adsorption degree were obtained at different flow rates: 95.89, 92.14 and 93.39%, at 0.00018, 0.0033 and 0.00027 dm^3 s^{-1}, respectively.[12–15] According to Fig. 3, it is also obvious that in all experimental series, Cu ions concentration is below the MAC value.

Adsorption of Zn cations is satisfactory for the lower flow rate. Values of 99.28 and 99.52% are calculated for the flow rates of 0.00018 and 0.00027 dm^3 s^{-1}, respectively. However, the value for the adsorption degree in the experimental series with flow rate of 0.0033 dm^3 s^{-1} is only 50.70% whereas the

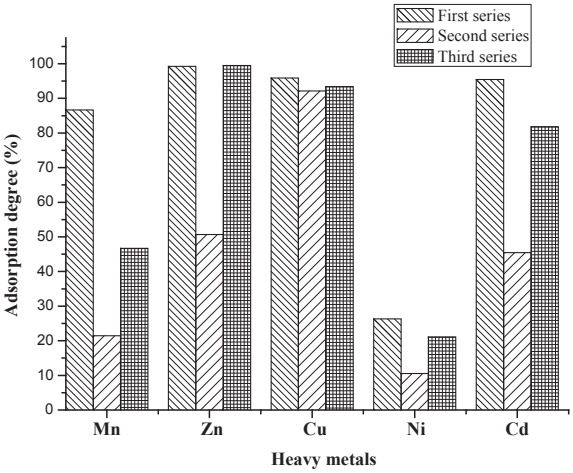

Fig. 2 Heavy metals adsorption degree.

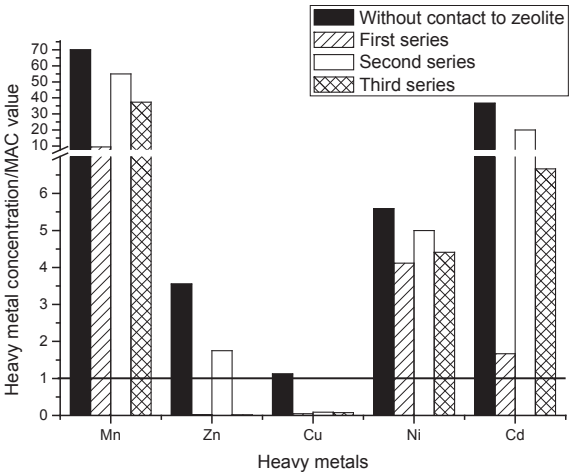

Fig. 3 Ratio of heavy metals concentration and corresponding MAC values.

output concentration it is higher than maximal allowable value according to the relevant legislation (Fig. 2).

For Mn, adsorption degree of 21.43% is the lowest reached at the flow rate of 0.0033 dm^3 s^{-1} that corresponds to expected value in real conditions (Fig. 2). Similar to the case of Zn, the results from Fig. 3 demonstrate that concentration of Mn ions in the effluent is higher than MAC value for all experiments.

Cd ions concentration upon purification is also higher than MAC value in all experimental series, (Fig. 3). It could be seen that the same values of adsorption degree is obtained for

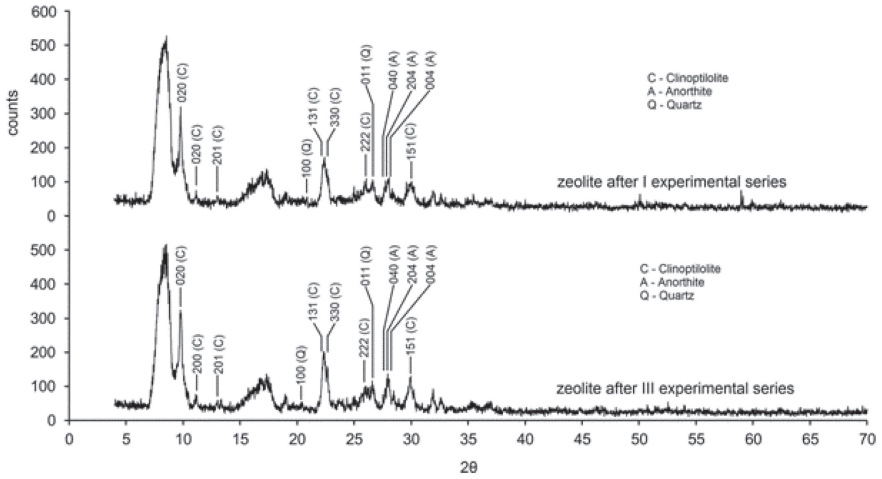

Fig. 4 X-ray diffraction patterns of natural zeolite samples after First and Third experimental series.

the flow rates of 0.00018 and 0.00027 $dm^3 s^{-1}$ (Fig. 2). The change in concentration is the lowest for the Ni ions. In this case, the adsorption degree is the similar for the all values of flow rate (Figs. 2 and 3).

Based on the data from the Figs. 2 and 3, the selectivity series for the removal the metal ions contained in the original AMD water could be defined at the flow rates of 0.00018, 0.0033 and 0.00027 $dm^3 s^{-1}$: Zn > Cu > Cd > Mn > Ni; Cu > Zn > Cd > Mn > Ni and Zn > Cu > Cd > Mn > Ni, respectively. These results are in accordance with other published results.[5,12–15] The adsorption capacity of the natural zeolite for heavy metal ions in treated AMD may be different due to a number of factors: hydration radii, hydration enthalpies, solubility of the cations. The hydration radii for the some characteristic cations are: $r_H Zn^{2+} = 4.30$ Å, $r_H Cu^{2+} = 4.19$ Å and $r_H Mn^{2+} = 4.38$ Å.[5] The heavy metal cations are presents hexaaqua complex ions with six surrounding water molecules in the solution and they passed the channel of zeolite in this form. Since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation are the same (+2). In ideal conditions; the smallest cations should ideally be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure. Therefore Mn^{2+} ions (the biggest diameter) have the minimum adsorption for the all tests, and Cu^{2+} ions (the least diameter) have maximum adsorption. Furthermore, adsorption should be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts with the adsorbent. Therefore, the hydration enthalpy is the stronger if the cation is more hydrated and the possibility of interaction with the adsorbent is less. Also, divalent cations with low hydration energies are sobbed preferably compared to cations with high hydration energies: −2010, −1955 and −1760 kJ mol^{-1} for Cu^{2+}, Zn^{2+}, Mn^{2+}, respectively.

The comparative XRD analysis was done with the aim to determine the change in the phase composition of the zeolite samples (−1 + 0.3 mm) upon adsorption of heavy metal ions from AMD in the first and third experimental series if any.

Table 4 Typical reflection for the zeolte samples.

No.	*hkl*	Zeolite Start	Zeolite I	Zeolite III
		d, Å		
		Clinoptilolite		
1	020	9.02	9.03	8.99
2	200	7.92	7.94	7.90
3	201	6.79	6.79	6.77
4	131	3.975	3.980	3.972
5	330	3.957	3.959	3.960
6	222	3.422	3.427	3.419
7	151	2.979	2.985	2.981
		Anorthite		
1	040	3.213	3.222	3.209
2	204	3.198	3.205	3.192
3	004	3.191	3.189	3.178
		Quartz		
1	100	4.26	4.25	4.25
2	011	3.343	3.344	3.342

The characteristic values are in accordance with the published results[16] and presented in Table 4.

The results of XRD analysis of natural samples after first and third experimental series are presented on Fig. 4.

The values for typical reflections (d-values), of minerals clinoptilolite, anorthite and quartz do not differ much for Zeolit Start, Zeolit I and Zeolit III samples. Crystal structure of the used zeolite did not change after the purification of the real AMD samples.

4. Conclusion

The investigation of AMD purification with natural zeolite samples was carried out in laboratory conditions using dynamic method. AMD flow rates were different for the three experimental series. The value of 0.0033 $dm^3 s^{-1}$ is close to the expected flow rate at real condition in industrially relevant environment. The results confirmed that, in the real conditions, natural zeolite can be used as an effective sorbent

only for Cu ions. The content of other heavy metal ions have been decreased, but the concentrations of metal ions upon purification are higher than maximal allowable concentration by actual legislation. It is defined that the own unique selectivity series for the metal ions contained in the AMD for the flow rate of 0.00018, 0.0033 and 0.00027 $dm^3 s^{-1}$ are: Zn > Cu > Cd >Mn > Ni; Cu > Zn > Cd > Mn > Ni and Zn > Cu > Cd > Mn > Ni, respectively. Also, it is defined that on the same order of flow rate magnitude the selectivity series for the metal ions are the same.

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